

The Effect of 0.1 Atomic Percent Zirconium on the Cyclic Oxidation Behavior of β -NiAl for 3000 Hours at 1200 °C

(NASA-TM-101408) THE EFFECT OF 0.1 ATOMIC
PERCENT ZIRCONIUM ON THE CYCLIC OXIDATION
BEHAVIOR OF β -NiAl FOR 3000 HOURS AT 1200
°C (NASA) 19 p CSCL 11P

N89-13566

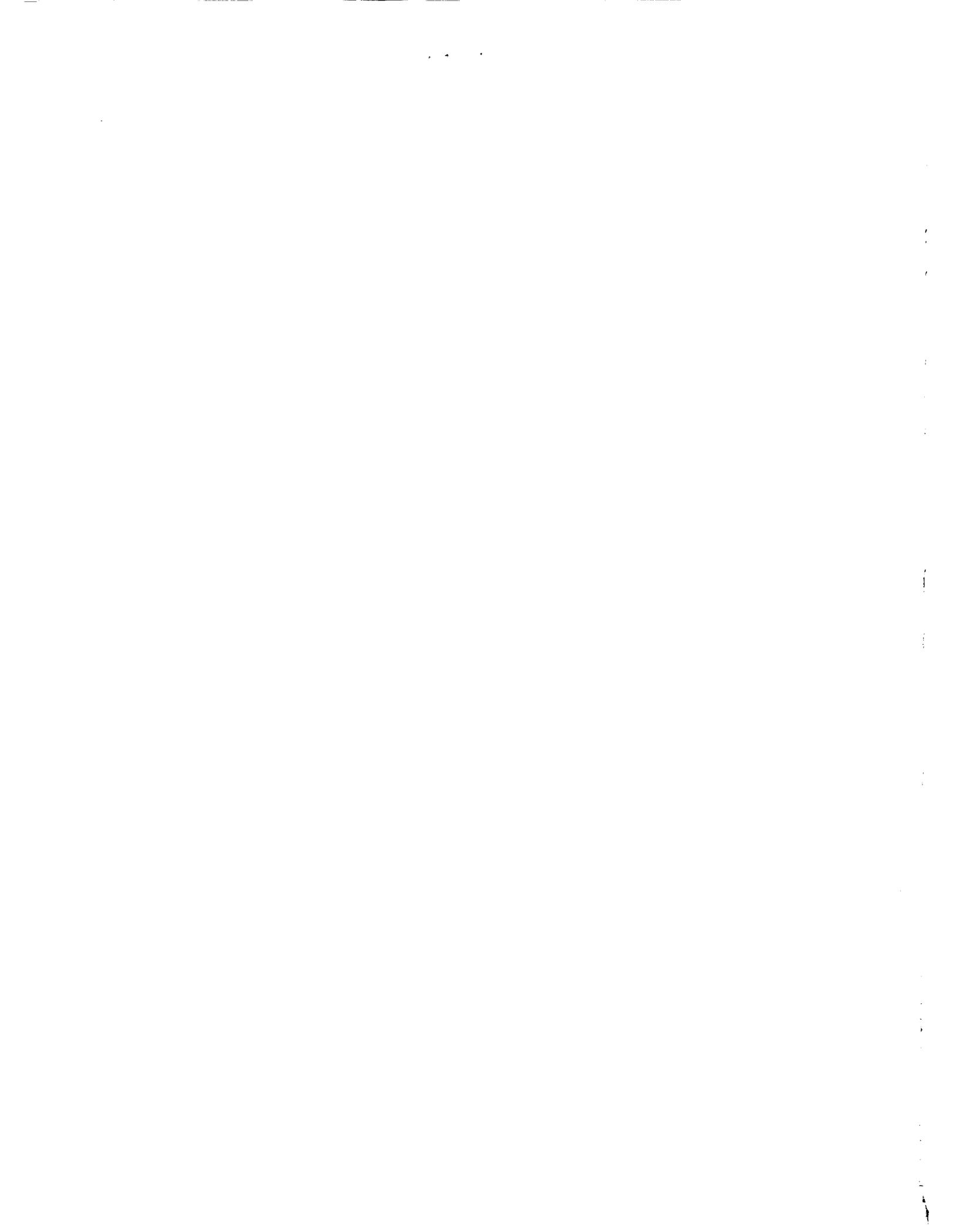
Unclass

G3/26 0179672

C.A. Barrett
*Lewis Research Center
Cleveland, Ohio*

Prepared for the
Workshop on the Oxidation of High-Temperature Intermetallics
sponsored by the Cleveland Chapter of ASM International and NASA Lewis
Research Center in cooperation with Case Western Reserve University, The
Metallurgical Society of AIME, and the Cleveland Chapter of TMS-AIME
Cleveland, Ohio, September 22-23, 1988

NASA



THE EFFECT OF 0.1 ATOMIC PERCENT ZIRCONIUM ON THE CYCLIC OXIDATION

BEHAVIOR OF β -NiAl FOR 3000 HOURS AT 1200 °C

C.A. Barrett
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

E-4366

The long time effect of 0.1 at % Zr (0.2 wt % Zr) on the cyclic oxidation behavior of hipped β -NiAl was studied. Oxidation testing was performed in static air at 1200 °C for up to 3000 1-hr exposure cycles. Specific weight change versus time data was modeled with the COSP computer program to analyze cyclic oxidation behavior. The Zr-free stoichiometric alloy oxidized and spalled randomly to bare metal between cycles at a rate high enough to deplete Al to a low enough level that oxidation "breakaway" took place as nonprotective NiO replaced the α -Al₂O₃/NiAl₂O₄ scale as the controlling oxide. The Zr minimized this severe type of spalling maintaining the protective α -Al₂O₃ scale even out to 3000 hr for the stoichiometric alloy with no significant Al depletion. A third β -NiAl alloy containing 0.1 at % Zr but with 10 percent less Al than the stoichiometric alloy was also tested and showed some depletion of Al, but the protective Al₂O₃/NiAl₂O₄ was still maintained to close to 2700 hr.

Introduction

A recent report from this laboratory detailed the effect of 0.2 wt % Zr in Beta-Nickel Aluminate (β -NiAl) on the cyclic oxidation behavior in air in the 1100 to 1200 °C temperature range (1). The Zr not only greatly increased the spall resistance of the α -Al₂O₃ formed on the alloy as it cooled down between heating cycles but also changed the nature of the spalling process. Without the Zr the protective α -Al₂O₃ spalls randomly at a high rate to bare metal. With Zr and its forming of ZrO₂ in the α -Al₂O₃ presumably a very thin fraction of the scale flakes off within the oxide after each cycle at a low rate. A computer program termed COSP was used to model the specific weight change time data based on these two processes to derive the oxide growth and spalling parameters as well as estimates of the metal consumed as total oxide at any given time. It was also shown by microprobe analysis that with Zr the alloy shows no significant Al gradient while the Zr free alloy shows a sizable linear Al gradient indicating large Al metal loss due to the spalling.

It was inferred from this earlier study that the Zr-free β -NiAl would eventually form NiO and "breakaway" when the Al level at the metal-oxide interface reached a critical level. In oxidation terms this is usually defined as failure since the protective Al₂O₃ no longer controls either the scale growth or scale spalling processes.

The purpose of this study was to extend the test time to a full 3000 1-hr cycles at 1200 °C in static air. This was to observe the anticipated failure process (i.e., breakaway) for the three β -NiAl alloys examined earlier. The alloys tested are described in Table I along with their fabrication history. They represent stoichiometric β -NiAl with and without 0.1 at % (0.2 wt %) Zr and a lean β -NiAl just within the beta region also containing 0.1 at % (0.2 wt %) Zr.

Specific weight change/time data will be generated as well as x-ray diffraction data at selected times. The NASA Lewis Research Center's Computer Program COSP will be used to model the weight change kinetics with emphasis on the change in scale control from protective Al₂O₃ initially, to the final unprotective NiO. COSP will also be used to compute the most important corrosion parameter - the metal consumed in the total oxidation process, W_m , as a function of time.

TABLE I. - β -NiAl ALLOYS-Zr EFFECT

[1/2 in. diameter disk samples -
machined from HIPped/PM rod alloy
powders placed in 4x3/4 in. S.S.
tube capsules HIPped 2350 °F at
20 000 psi for 2 hr.]

Alloy	
1	Ni-46.6 at % Al-0. at % Zr (-28.6 wt % Al-0. wt % Zr)
2	Ni-48.3 at % Al-0.1 at % Zr (-30.0 wt % Al-0.2 wt % Zr)
3	Ni-38.1 at % Al-0.1 at % Zr (-22.0 wt % Al-0.2 wt % Zr)

Procedure

The three β -NiAl alloy powder compositions studied were obtained from Alloy Metals, Inc. of Troy, Michigan two of which contained ~0.2 wt % Zr. The alloy powders were placed in 4 in. long by 3/4 in. diameter stainless steel tube capsules and HIPped at 1288 °C (2350 °F) and 20 000 lb for 2 hr. The resulting rod was trimmed and machined into small disk coupons with a small hanger hole drilled for hanging during cyclic oxidation testing. Table I summarizes the chemistry of the three alloys tested. The three PM/HIPped alloys were denoted as alloys 1, 2, and 3 as indicated in Table I. Alloy 1 contains no Zr while alloy 3 has a significantly lower Al level that is just within the single phase β -NiAl region at 800 °C. Alloys 1 and 2 were essentially stoichiometric β -NiAl.

These three alloys were tested together in cyclic oxidation at 1200 °C in static air for up to 3000 1-hr cycles in a standard NASA Lewis cyclic oxidation rig (2). The alloys were examined at selected intervals using x-ray diffraction to determine the oxide phases that formed within the scale. Post-test SEM and microprobe analyses were also performed on selected samples. The original microstructures have been discussed in Ref. 1.

Results and Discussion

The specific weight change versus time data for 1 hr cycles are listed in Table II and plotted in Figs. 1 and 2. Figure 1 shows all three alloys plotted together. Because the Zr-free alloy 1 shows such a drastic specific weight loss the differences between the Zr containing alloys, the stoichiometric alloy 2 and the leaner beta alloy 3, are not apparent until plotted on a smaller scale shown in Fig. 2. The Zr free alloy $\Delta W/A$ values drop steadily with time as the alloy continuously spalls with each cycle. The alloy 1 samples appear at any given time during roughly half of the 3000 hr test to be metallic (i.e., nearly bare of scale) then becoming more scaled and wrinkled with time with severe edge attack. The Zr containing stoichiometric alloy 2 maintains a thin, tightly adherent dark gray scale with negligible spall with no distortion even out to 3000 hr. Alloy 3 behaves similarly but has a lighter gray scale. At 3000 cycles alloy 3 shows a slight amount of distortion. Alloy 1 was removed from test at 2500 and 2600 hr because of severe sample distortion.

Post-Test Analysis

X-ray analyses of the sample surfaces and any collected spall are summarized in Table III after various times and at the end of the tests for all three alloy samples. Even though alloy 1 is obviously spalling it could not be collected in the spall catcher cups until 2000 hr and after because it was so fine that it was dispersed in air. Until 1500 hr α -Al₂O₃ is found as the surface oxide on alloy 1. Thereafter both nickel aluminate and NiO are detected. Alloy 2 uniformly forms α -Al₂O₃ with trace ZrO₂ on the surface. Any spall is α -Al₂O₃ detected after 1500 hr with possible aluminate spinel and trace ZrO₂ at later times. The lower Al alloy 3 behaves similarly to alloy 2 until 1500 hr when nickel aluminate is detected. The spall shows some NiO at 2500 hr.

TABLE II. - SPECIFIC WEIGHT CHANGE DATA-1200 °C mg/cm² 1 HR
EXPOSURE CYCLES STATIC AIR-β-NiAl

Time, hr	Alloy 1: Ni-46.6%Al-0.Zr		Alloy 2: Ni-48.3%Al-0.1%Zr	Alloy 3: Ni-38.1%Al-0.1%Zr	
	683-4	683-5	683-2	683-3	683-6
1	0.31	.31	0.20	0.22	0.25
15	-.28	-.39	.64	.81	.84
30	-.84	-1.04	.89	1.09	1.12
45	-1.57	-2.04	1.03	1.23	1.29
60	-2.38	-2.88	1.17	1.40	1.43
75	-3.05	-3.42	1.20	1.51	1.57
90	-4.11	-4.79	1.31	1.62	1.68
100	-4.87	-5.54	1.43	1.71	1.76
115	-5.76	-6.49	1.48	1.68	1.74
130	-6.83	-7.61	1.57	1.74	1.82
145	-8.06	-8.90	1.62	1.79	1.85
160	-9.09	-10.05	1.59	1.79	1.88
175	-10.35	-11.31	1.65	1.82	1.90
190	-11.53	-12.43	1.68	1.82	1.90
200	-12.23	-13.24	1.79	1.88	1.93
250	-15.45	-16.65	1.87	1.90	1.96
300	-19.28	-20.71	1.98	2.02	2.02
350	-23.42	-24.99	2.01	2.02	2.02
400	-27.56	-29.28	2.12	2.07	2.07
450	-31.95	-33.84	2.07	2.02	1.93
500	-36.21	-38.37	2.12	2.04	1.90
550	-40.82	-43.05	2.12	1.88	1.71
600	-45.30	-47.44	2.18	1.90	1.76
650	-49.55	-51.58	2.07	1.90	1.71
700	-53.47	-55.19	2.07	1.90	1.74
750	-56.75	-58.33	2.04	1.88	1.71
800	-59.74	-60.96	1.98	1.85	1.68
850	-62.48	-63.31	1.93	1.88	1.65
900	-65.11	-65.55	1.87	1.82	1.65
950	-66.54	-66.61	1.79	1.74	1.60
1000	-67.60	-67.17	1.71	1.65	1.51
1100	-68.83	-67.73	1.54	1.46	1.29
1200	-68.47	-66.19	1.43	1.26	1.06
1300	-67.49	-65.30	1.26	1.09	.81
1400	-69.14	-68.96	1.06	.70	.42
1500	-74.32	-75.71	.81	.36	0.0
1600	-82.85	-84.86	.45	-.76	-1.09
1700	-92.17	-95.80	.28	-1.09	-1.57
1800	-102.61	-108.03	.03	-1.74	-2.16
1900	-112.74	-122.00	-.20	-2.41	-2.97
2000	-126.14	-138.34	-.42	-3.19	-3.98
2100	-153.50	-157.18	-.87	-4.71	-5.40
2200	-191.89	-193.73	-1.09	-5.24	-5.94
2300	-231.54	-243.66	-1.37	-5.91	-6.75
2400	-257.96	-270.33	-1.59	-6.58	-7.39
2500	-286.44	-296.50	-1.82	-7.14	-7.90
2600	-310.31	-----	-2.18	-----	-9.44
2700	-----	-----	-2.40	-----	-10.30
2800	-----	-----	-2.66	-----	-13.05
2900	-----	-----	-2.85	-----	-16.35
3000	-----	-----	-3.08	-----	-18.20

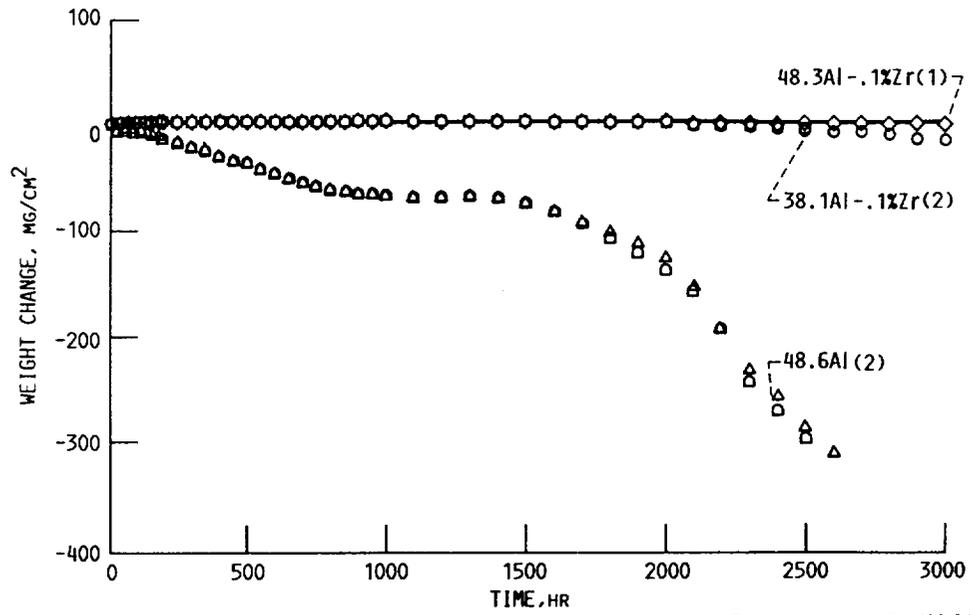


Figure 1. - Specific weight change/time data for three β -NiAl alloys tested at 1200 °C, 1-hr exposure cycles in static air.

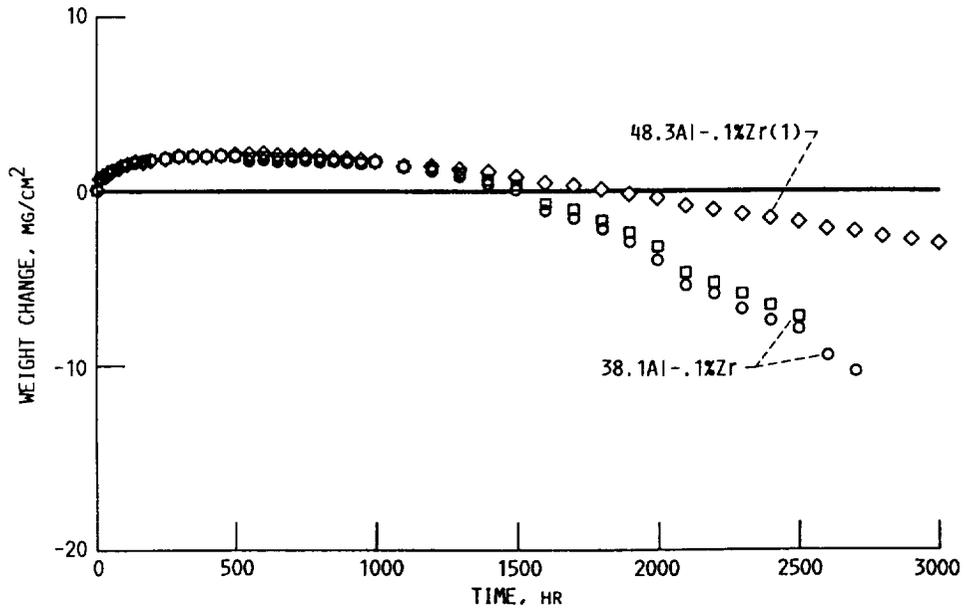


Figure 2. - Specific weight change/time data for the two Zr containing β -NiAl alloys tested at 1200 °C, 1-hr exposure cycles in static air.

TABLE III. - X-RAY DIFFRACTION RESULTS FOR HIPPED β -NiAl ALLOYS TESTED FOR 1-HR EXPOSURE CYCLES
IN STATIC AIR AT 1200 °C

[Phases listed in decreasing order of intensity. Code: A = α Al₂O₃; Z = ZrO₂; S = Nickel aluminate spinel;
a₀ = 8.05 to 8.10 Å; N = NiO; β -NiAl matrix as weakest surface phase under oxides.]

Alloy	Run	Oxide surface phases present at various times, hr										Spall-when observed
		1	100	200	500	1000	1500	2000	2500	3000		
Alloy 1 Ni-46.6%Al-0.1%Zr	683-4	A	A	A	A	A ^a	A, S, Nb	A, SC	S, N, Ad	-----	2000 hr-A, S 2500 hr-N, S, A	
	683-5	A	A	A	A	A ^a	A, S, Nb	A, SC	S, N, Ad	-----	2000 hr-A, S 2500 hr-N, S, A	
Alloy 2 Ni-48.3%Al-0.1%Zr	683-2	A	A, Z	A, Z	A, Z	A, Z	A, Z	A, Z	A, Z	A, Z	1500 hr-A 2000 hr-A, S, Z 2500 hr-A	
	683-3	A	A, Z	A, Z	A, Z, S	A, Z	A, Z, S	A, S, Z	A, Z, S	-----	1500 hr-A 2000 hr-A, S, Z 2500 hr-A, Z, S	
Alloy 3 Ni-38.1%Al-0.1%Zr	683-6	A	A, Z	A, Z	A, Z, S	A, Z	A, Z, S	A, Z, S ^b	A, Z, S	A, S, Z ^c	1500 hr-A 2000 hr-A, S, Z 2500 hr-N, S, A	

^aMartensitic β -NiAl under scale

^b β -NiAl and γ' Ni under scale

^c γ' Ni under scale

^d γ' Ni and β -NiAl under scale

Metallography, SEM, and Electron Microprobe Analysis Results

The microstructure of the three alloys were compared at 2500 and 3000 hr where possible.* The severely distorted alloy 1 was examined only after 2500 hr. It showed a severely convoluted surface with massive oxide penetration. Alloy 2 at both times show a coherent scale with slight penetration and a uniform beta matrix. The lower Al alloy 3, however, shows a more intrusive, thicker scale at both times and at 3000 hr part of the metallic layer under the scale appears to be γ' due to Al depletion.

Electron microprobe analyses were performed on the three alloys at 2500 hr and for alloys 2 and 3 at 3000 hr. Traces were made for Ni, Al, and Zr. As was shown in Ref. 1 the gradients were all linear from the center of sample. The most important parameter is the Al level at the metal-oxide interface. Table IV summarizes these results along with the results from Ref. 1. It shows that at 1100 °C even after 3000 1-hr cycles there is no significant Al depletion for any of the three alloys. At 1150 °C this is also true after 3000 1-hr cycles for Zr containing alloys 2 and 3. For the Zr-free alloy 1 the linear gradient goes from 29 to 23 wt % Al. At 1200 °C alloy 1 drops to 20 wt % after 500 hr and 8 wt % after 2500 hr. This drop coincides with the formation of NiAl_2O_4 , then NiO . Alloy 2 still shows only a 1 percent drop in Al content after 3000 hr maintaining the $\alpha\text{-Al}_2\text{O}_3$ protective scale. Alloy 3, however, with the lower starting Al content of 22 to 23 wt % Al is more prone to change from $\alpha\text{-Al}_2\text{O}_3$ to NiAl_2O_4 with just a 2 to 3 percent drop in Al at the metal-oxide interface. Some nonprotective NiO is apparently formed as well near 2500 hr.

*Alloy 2 sample 683-1 was also tested to 2500 hr along with 680-2 which was tested to 3000 hr. It gave invalid $\Delta W/A$ results however, because a small oxide dimple was formed on a small imperfection on the test sample. The rest of the sample was similar, however.

TABLE IV. - $\beta\text{-NiAl}$ ALLOYS-Zr EFFECT

[Final Al surface content-wt % -
microprobe data.]

Alloy	Time, hr	Temperature, °C		
		1100	1150	1200
		Final Al content, wt %		
Alloy 1: 29Al	500	--	--	20
	2500	--	--	8
	3000	30	23	--
Alloy 2: 30Al(Zr)	500	--	--	30
	2500	--	--	29
	3000	31	30	29
Alloy 3: 22Al(Zr)	500	--	--	23
	2500	--	--	21
	3000	23	23	20

Figures 3(a) to (c) shows the back scattered electron micrographs for the 3 alloys at the longest time they were tested at 1200 °C. The light areas indicate the higher atomic number regions (i.e., base metal). The darker areas show the areas of lower atomic number (i.e., oxides). This confirms the tendency of the Zr-free alloy to spall to base metal as well as to form massive NiO. Alloy 1 appears many layered while alloy 2 appears quite uniform.

Scanning electron micrographs are shown in Fig. 4(a) to (c) for the same samples at the times described above. Alloy 1 again shows spalling to base metal typified by dimples, crystallographic voids and imprints of the oxide grains. Alloy 2 is of interest because it still shows remnants of the protective lacey oxide ridge structure of α -Al₂O₃ described by Doychak (3).

Cyclic Oxidation Computer Model

The computer program COSP was developed at NASA Lewis in an attempt to model the cyclic oxidation process that involves the interaction between scale growth and scale spalling. This approach has been detailed in Refs. 1, and 4 to 6 and is based on the mass balance equation at any time, t

$$\Delta W/A = W_r - W_m \quad (1)$$

where $\Delta W/A$ is any of the specific weight change values cited previously-experimental data versus time, W_r is the specific weight of oxide formed on the specimen after cooling to ambient temperature after spalling, and W_m the amount of metal consumed in the total oxidation process up to time, t.

Further the specific amount of spall during any cycle is defined as

$$W_s = W'_r - W_r \quad (2)$$

where W'_r is the specific weight of the oxide on the metal at time, t prior to spalling during that cycle. The purpose of the COSP program is to try to match the $\Delta W/A$, time curve values for a cyclic oxidation program run for a given alloy sample run at a particular test temperature-cycle by cycle for a fixed cycle time. For these runs these are for 1 hr cycles.

These values are computed by the COSP program using the critical parameters defining scale growth and scale spalling. In this case the scale growth constants are k_p , the parabolic scaling constant which determines the rate of scale growth and a_s a stoichiometric constant which defines the type of scale growth. These two constants can usually be easily derived - the k_p from isothermal gravimetric tests and the a_s values by determining the oxide formed by x-ray analysis.

The actual cyclic process involves oxidation to form a scale which thickens by diffusional growth. As the sample cools the oxide spalls, thus reducing the oxide thickness, possibly to bare metal. As the sample returns to temperature, growth continues as before but the growth rate is that corresponding to the reduced scale thickness (i.e., the growth rate is increased). In the case of parabolic growth this is simply a projection back to an earlier part of the growth curve or in the case of spalling to bare metal to the beginning of scale growth curve where its slope (i.e., instantaneous scaling rate) is highest. In the case of the aluminide alloys tested here, the growth rates are parabolic. Therefore, after spalling the rate is assumed to continue to follow the initial or previous growth

ORIGINAL PAGE IS
OF POOR QUALITY.

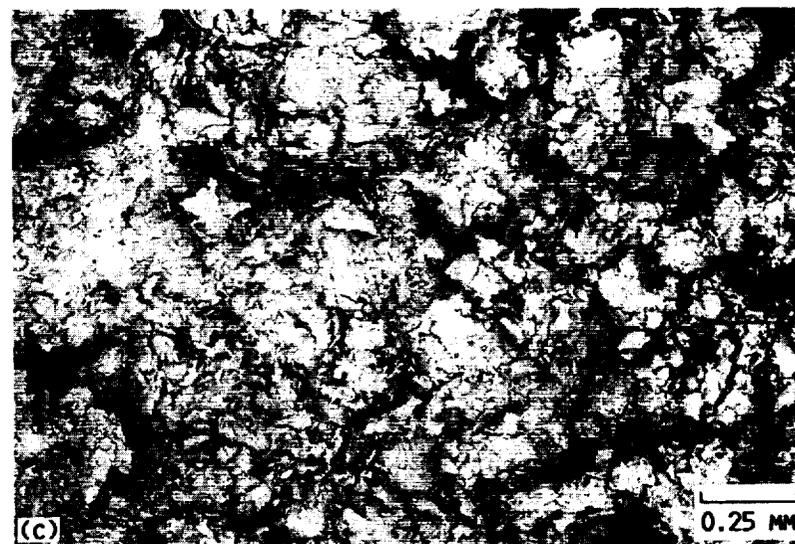
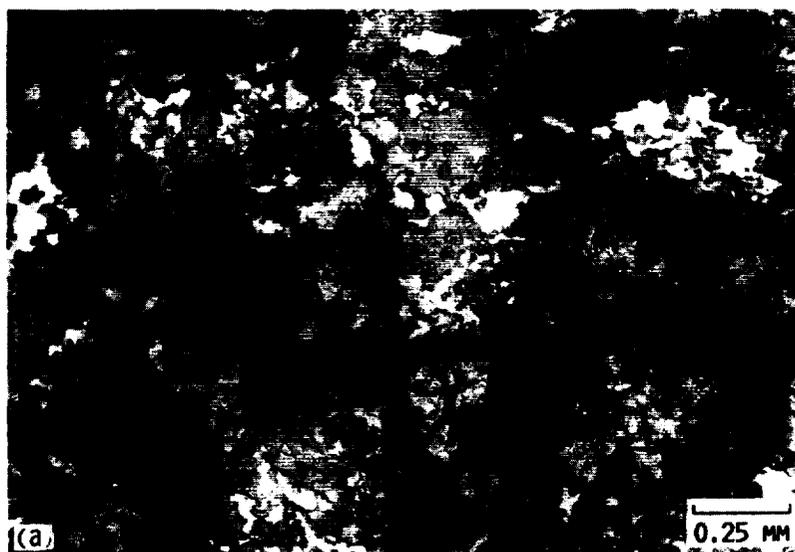


Figure 3. - Back scattered scanning electron microscopy at of the three β -NiAl alloys run at 1200 °C shown at the longest time tested, 1-hr exposure cycles in static air. (3a alloy 1, 2600 hr; 3b alloy 2, 3000 hr; 3c alloy 3, 3000 hr).

ORIGINAL PAGE IS
OF POOR QUALITY.

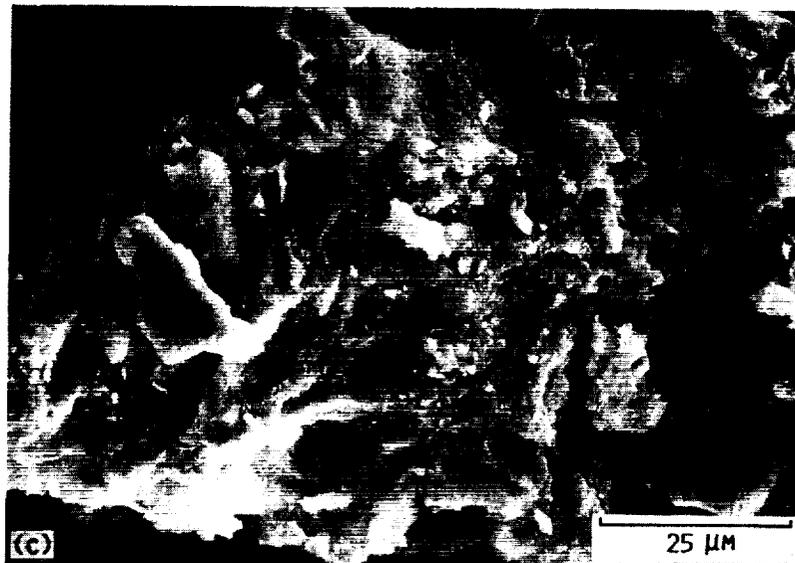
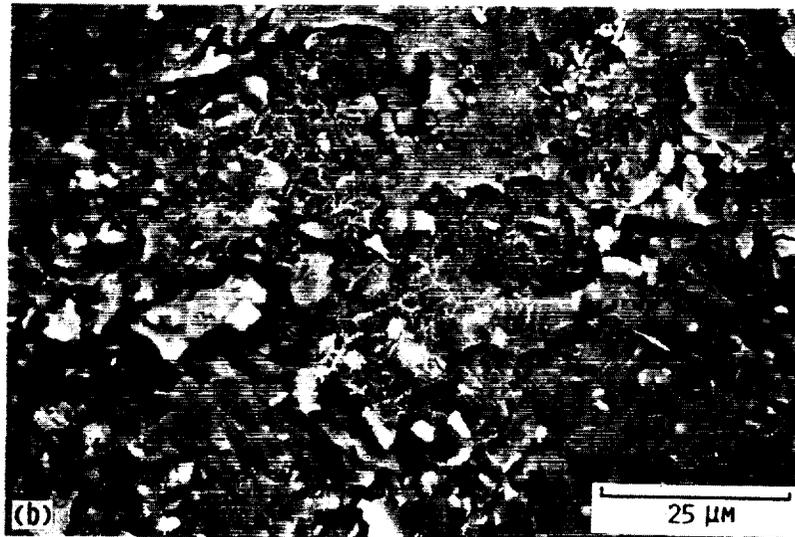
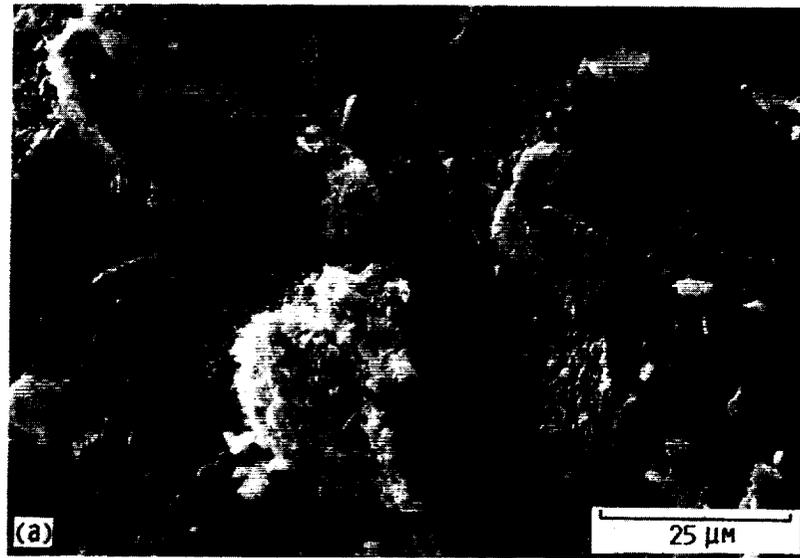


Figure 4. - Detail of surface oxide morphology of the three β -NiAl alloys run at 1200 °C shown at the longest time tested, 1-hr exposure cycles in static air. (4a alloy 1, 2600 hr, 3b alloy 2, 3000 hr; 3c alloy 3, 3000 hr).

curve even though the effective time could be considerably less than the actual test time. The remaining problem is to model the spalling process. As was shown in Ref. 1 the Zr containing alloys spall according to

$$W_s = Q_0 (W_r')^2 \quad (3)$$

where Q_0 is the probability coefficient of spalling. Thus as the scale thickness increases the amount of spall increases.

Q_0 can be measured independently but because the values for commercial Al_2O_3 formers are generally so low very large surface areas are required. Although experimentally difficult, ranges of values can be inferred and used in Eq. (3) in COSP to match the experimental gravimetric/time cyclic curves. Special cases of this process occur when spalling to bare metal takes place (i.e., $W_s = W_r'$). In the COSP program a square centimeter is broken into up to 1000 segments. Individual segments are followed for each cycle where spalling takes place by either spalling to bare metal or not spalling at all. In the spalling to bare metal case S_0 is used instead of Q_0 to indicate the spalling probability. In the simplest case a rectangular distribution is used with a random number generator. If the random number is normalized all values below the critical spalling probability, S_0 will result in spalling to bare metal; above S_0 no spalling occurs. This process is followed for each segment for each cycle throughout the entire length of the test. This COSP computer program also computes other critical parameters as a function of time, particularly W_m , which is the critical value in any corrosion process, W_r , cross-over times, etc.

Figure 5 shows this computation process for the COSP program using model 2 for the Zr containing alloys 2 and 3 and the random spalling to bare metal model 5 for alloy 1. For the tests detailed in Ref. 1 the curve matches were considered good to excellent.

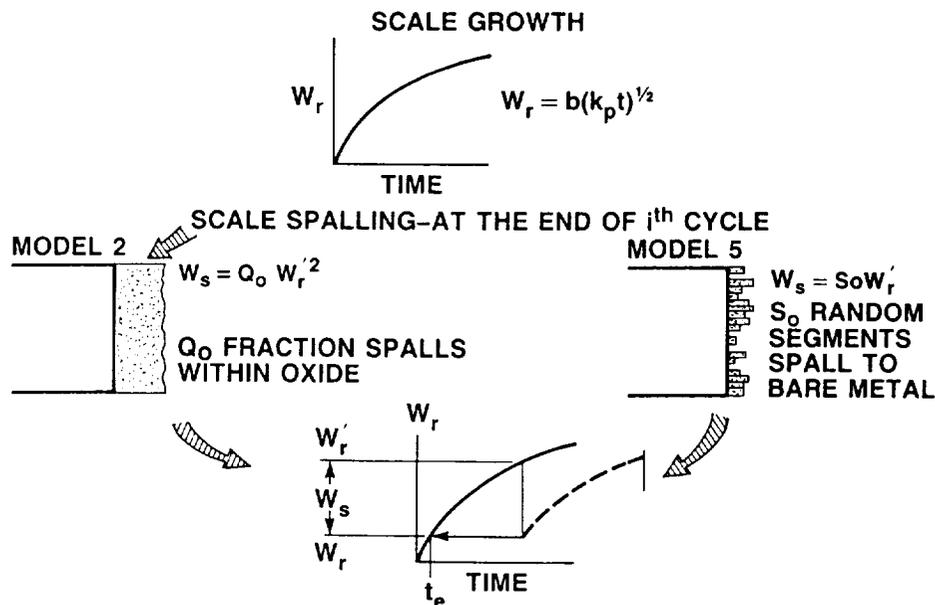


Figure 5. - Schematic diagram of the COSP computer modeling program for the cyclic oxidation/spalling process applied to β -NiAl alloys with Zr (model 2) and without Zr (model 5).

Of the 5 individual $\Delta W/A$, time curves plotted on Fig. 1 only alloy 2 run to 3000 hr (run 683-2) resemble the classic parabolic shape curves that can be easily fitted by COSP. It was assumed the change in shape of the other 4 curves particularly those for alloy 1 was due to a second and then possibly a third oxide becoming rate controlling. On this basis the COSP program was modified by a "trigger" mechanism that allowed the critical input values to be changed at any given time to match the growth and spalling characteristics of a given controlling oxide. The only limitation is that the spalling model itself does not change (i.e., if a sample once spalls randomly in segments it continues to do so).

Figure 6 along with Table V indicates schematically how this modelling process is carried out. Alloy 1 (683-5) is shown. The initial controlling oxide is $\alpha\text{-Al}_2\text{O}_3$ which scales parabolically with a k_p of 0.0200 (1) and a stoichiometric constant, a_s of 1.1242. The earlier study on this alloy which was terminated after 1000-1 hr cycles at 1200 °C was shown to spall randomly to bare metal with an S_0 (spalling probability) of 25 percent. At position (2) this $\alpha\text{-Al}_2\text{O}_3$ control ended at 800 hr after a transition region of 50 hr nickel aluminate (NiAl_2O_4) took over at 850 hr, (3) with an a_s value of 1.7604. There is no valid k_p for aluminate scale control but it is assumed to be slightly higher than that for $\alpha\text{-Al}_2\text{O}_3$ (see Table II, early time data). On this basis a value for k_p of 0.0300 was used. To match the flattened curve in this region S_0 was found to be equal to 0.02. This process continues until 1500 hr, position (4). At this point transition to NiO control begins and the $\Delta W/A$ values start to drop drastically which can be considered "breakaway" (i.e., failure). NiO control is complete at 2100 hr. When NiO takes over the scaling rate is still assumed to be parabolic with its a_s value of 3.6694. k_p values in the literature for pure nickel in various forms at 1200 °C ranges from 1.0 to about 3.0 (6). Here a k_p value of 2.0 was used arbitrarily. The spalling probability was found to be roughly 5 to 10 percent as is indicated by SEM back scattering results.

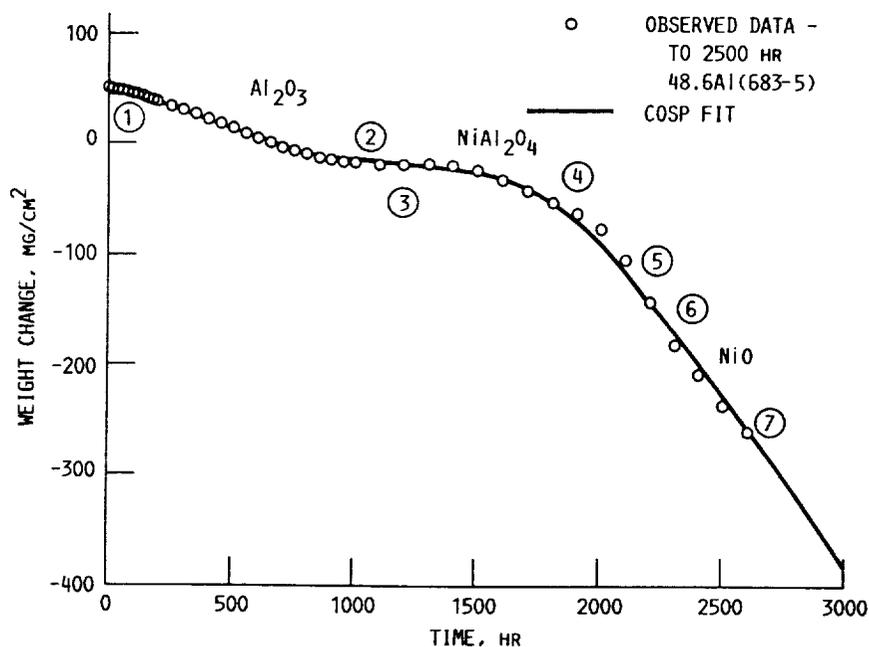


Figure 6. - COSP computer modeling fit for alloy 1 (run 683-5) showing "trigger" positions for oxide control using input from table V.

TABLE V. - Zr EFFECT β -NiAl (HIPPED/PM)

1200 °C, 1-HR CYCLES

[COSP input (683-5), Model 5, 400 segments.]

NTRIG = 6					
Pos	Time	Oxide	k_p	S_o	A_s
1	0	Al ₂ O ₃	0.0200	0.25	1.1242
2	800	Al ₂ O ₃	.0200	.25	1.1242
3	850	NiAl ₂ O ₄	.0300	.02	1.7604
4	1500	NiAl ₂ O ₄	.0300	.02	1.7604
5	2100	NiO	2.00	.05	3.6694
6	2200	NiO	2.00	.042	3.6694
7	2500	NiO	2.00	.042	3.6694

The same approach was taken for all 5 runs. Table VI summarizes the input constants for the three types of scale control where applicable. Figure 7 shows the observed data and matching COSP fit for alloy 2 (683-2). Here model 2 with α Al₂O₃ controls throughout the entire run with only a small specific weight loss after 3000 cycles. The spalling probability coefficient is a very low 0.000084. This is confirmed by the various post-test analyses.

TABLE VI. - β -NiAl-Zr EFFECT - 1200 °C STATIC AIR, 3000 1-HR CYCLES - CHANGE IN SCALE CONTROL

Alloy	Run	Time, hr	I-Al ₂ O ₃ control	II-NiAl ₂ O ₄ control	III-NiO control
Alloy 1: 46.6Al-0.Zr	683-4	0-2600	0-800 hr $k_p = 0.0200$ $S_o = 0.25$	850-1500 hr $k_p = 0.0300$ $S_o = 0.02$	2100-2600 hr $k_p = 2.00$ $S_o = .05$ to .034
	683-5	0-2500	0-800 hr $k_p = 0.0200$ $S_o = 0.25$	850-1500 hr $k_p = 0.0300$ $S_o = 0.02$	2100-2500 hr $k_p = 2.00$ $S_o = .05$ to .042
Alloy 2: 48.3Al-.1Zr	683-2	0-3000	0-3000 hr $k_p = 0.0200$ $Q_o = 0.000084$	-----	-----
Alloy 3: 38.1Al-.1Zr	683-3	0-2500	0-1400 hr $k_p = 0.0200$ $Q_o = 0.000100$	1500-2500 hr $k_p = 0.300$ $Q_o = 0.000300$	-----
	683-6	0-3000	0-1400 hr $k_p = 0.0200$ $Q_o = 0.000100$	1500-2600 hr $k_p = 0.0300$ $Q_o = 0.000400$	2700-3000 hr $k_p = .1000$ $Q_o = .001900$
	683-6	0-3000	-----	2700-3000 hr $k_p = .1000$ $Q_o = .001900$	-----

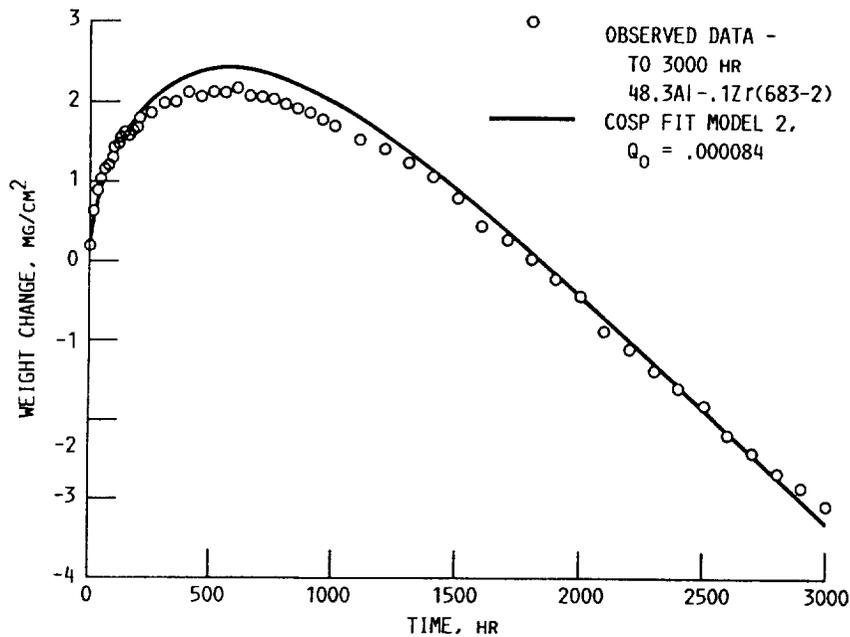


Figure 7. - Cosp computer modeling fit for alloy 2 (run 683-2).

Alloy 3 runs are more complex. The Cosp fit for sample 680-6 is shown in Fig. 8. Up to about 1400 hr $\alpha\text{Al}_2\text{O}_3$ controls with the same k_p of 0.0200 using model 2 but the Q_0 is slightly higher with a value of 0.000100. NiAl_2O_4 takes over in the 1500 to 2600 hr range with the same k_p as alloy 1 of 0.0300 but with Q_0 's of 0.000300 to 0.000400 respectively for the 2 runs. For sample 683-6 which was run to 3000 hr NiO appears near 2700 hr. The k_p value is assumed to increase slightly to .1. Q_0 , however, is still fairly low at 0.002 but the specific weight change drops sharply at 2600 to 2700 hr indicating possible breakaway. Again these tendencies are verified by x-ray diffraction, microprobe and SEM analyses. The duplicate of alloy 1 has a Cosp fit almost identical to that of Fig. 6.

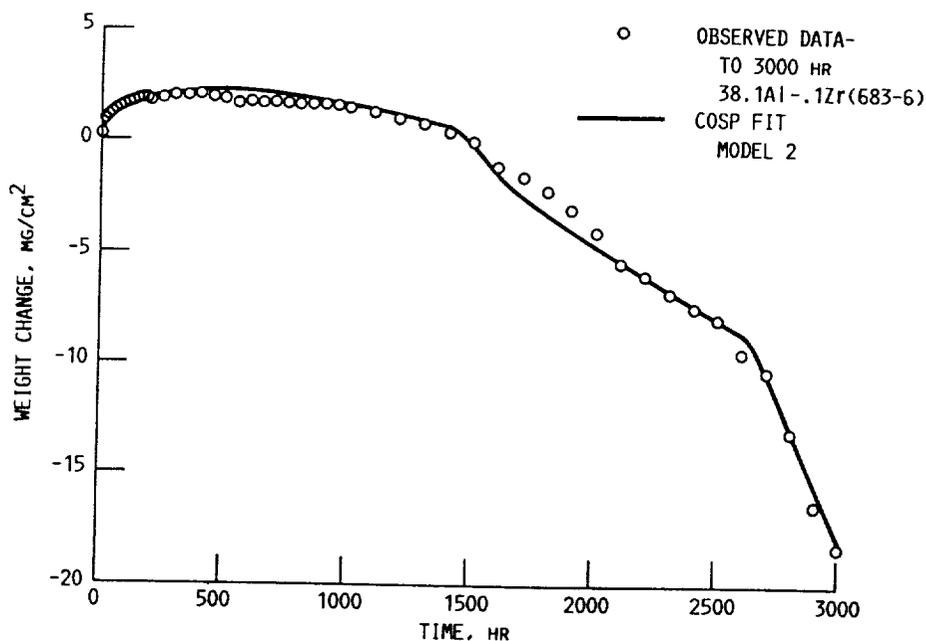


Figure 8. - Cosp computer modeling fit for alloy 3 (run 683-6).

The aim of this study was not only to infer the proper growth and spalling modes for the β -NiAl alloy with and without Zr during cyclic oxidation at 1200 °C but to derive accurate rate constants as well. In addition the amount of metal consumed, W_m at any time, t is the ultimate aim in any corrosion or oxidation study. It is implicit in any isothermal oxidation test (i.e., $W_m = a_s(k_p t)^{1/2}$) or in any corrosion study when a thickness change is measured in microns (for attack from one side):

$$W_m = \frac{\rho \cdot \Delta th}{10} \quad (4)$$

Here ρ is the average density of all the metals converted to oxide (Ref. 7). Table VII shows the computed W_m values along with the observed and calculated $\Delta W/A$ values based upon the input values listed in table for each run. A $\Delta W/A$ value - 5.0 mg/cm² for 100 hr is sometimes taken as a critical specific weight loss value (Ref. 8). On this basis the stoichiometric β -NiAl with Zr still has excellent cyclic oxidation resistance even at 3000 hr. The more critical W_m values showed in the table indicate the wide difference in metal consumption the Zr free stoichiometric β -NiAl was consumed nearly 70 times the amount of metal as the same alloy with the small amount of Zr. On the other hand the lower Al alloy with Zr has a metal consumption value four times that of the stoichiometric alloy with Zr.

TABLE VII. - Zr EFFECT - β -NiAl (HIPPED/PM) - 1200 °C, 1-HR CYCLES - COSP ESTIMATES

Alloy	Run	Time, hr	$\Delta W/A$ final	Final $\Delta W/A$ (calculated)	Final W_m (calculated)	Final oxide
Alloy 1: 46.6Al-0.Zr	683-4	2600	-310.31	-310.0	818.6	NiO
	683-5	2500	-296.50	-295.6	767.7	NiO
Alloy 2: 48.3Al-.1Zr	683-2	3000	-3.08	-3.30	11.41	α Al ₂ O ₃
Alloy 3: 38.1Al-0.1Zr	683-3	2500	-7.14	-6.81	16.25	NiAl ₂ O ₄
	683-6	3000	-18.20	-18.16	32.00	NiN ₂ O ₄ (NiO)

Concluding Remarks

Using COSP to model the cyclic oxidation process is reasonably straight forward in the case where a single oxide appears to control the kinetics. This was true in this study for the alloy 2, run 683-2. It is more controversial to model more complex runs such as for alloy 1. Although the fit appears to be excellent in matching the observed and computed $\Delta W/A$ values at the various times and the kinetic constants appear reasonable there is no independent check of the growth constants for NiAl₂O₄ and NiO when they control on alloys which initially form α Al₂O₃ as the protective oxide. The same is true for the spalling constants as well. They were derived basically by trial and error with the criteria that they give $\Delta W/A$ values that match the experimental values and that the constants are reasonable and that they are internally consistent (i.e., that the k_p for α NiAl₂O₄ is the same for all the alloys regardless of how they eventually spall.) On this basis COSP is a useful tool to examine complex cyclic oxidation kinetics but methods of independent verification should be developed as well.

References

1. C.A. Barrett: Oxid. Met., 1988, vol. 30, pp. 361-390.
2. C.A. Barrett and C.E. Lowell: J. Test. Eval., 1982, vol. 10, pp. 273-278.
3. J.K. Doychak: "The Evolution and Growth of Al₂O₃ Scales on Beta-NiAl," NASA CR-175097, 1986.
4. C.E. Lowell, J.L. Smialek, and C.A. Barrett: in High Temperature Corrosion, NACE-6, R.A. Rapp, ed., National Association of Corrosion Engineers, Houston, TX, 1983, pp. 219-226.
5. C.E. Lowell, et al.: "COSP: A Computer Program to Analyze Cyclic Oxidation," to be published.
6. H.B. Probst and C.E. Lowell: J. Met., 1988, vol. 40, no. 10, pp. 18-21.
7. C.E. Lowell, S.J. Grisaffe, and D.L. Deadmore: Oxid. Met., 1972, vol. 4, pp. 91-111.
8. R.A. Perkins, G.H. Meier, and K.T. Chiang: "Formation of Alumina on Niobium- and Titanium-Base Alloys," Paper presented at the Workshop on Oxidation of High-Temperature Intermetallic, sponsored by NASA Lewis Research Center, Case Western Reserve University, and the Cleveland Chapter of AIME, Cleveland, OH, Sept. 22-23, 1988.
9. C.A. Barrett and E.B. Evans: "Cyclic Oxidation Evaluation - Approaching Application Conditions," NASA TM X-68252, 1973.

1. Report No. NASA TM-101408		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle The Effect of 0.1 Atomic Percent Zirconium on the Cyclic Oxidation Behavior of β -NiAl for 3000 Hours at 1200 °C				5. Report Date	
				6. Performing Organization Code	
7. Author(s) C.A. Barrett				8. Performing Organization Report No. E-4366	
				10. Work Unit No. 505-60-01	
9. Performing Organization Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135-3191				11. Contract or Grant No.	
				13. Type of Report and Period Covered Technical Memorandum	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546-0001				14. Sponsoring Agency Code	
15. Supplementary Notes Prepared for the Workshop on the Oxidation of High-Temperature Intermetallics sponsored by the Cleveland Chapter of ASM International and NASA Lewis Research Center in cooperation with Case Western Reserve University, The Metallurgical Society of AIME, and the Cleveland Chapter of TMS-AIME, Cleveland, Ohio, September 22-23, 1988.					
16. Abstract The long time effect of 0.1 at % Zr (0.2 wt % Zr) on the cyclic oxidation behavior of hipped β -NiAl was studied. Oxidation testing was performed in static air at 1200 °C for up to 3000 one-hour exposure cycles. Specific weight change versus time data was modeled with the COSP computer program to analyze cyclic oxidation behavior. The Zr-free stoichiometric alloy oxidized and spalled randomly to bare metal between cycles at a rate high enough to deplete Al to a low enough level that oxidation "breakaway" took place as nonprotective NiO replaced the α -Al ₂ O ₃ /NiAl ₂ O ₄ scale as the controlling oxide. The Zr minimized this severe type of spalling maintaining the protective α -Al ₂ O ₃ scale even out to 3000 hours for the stoichiometric alloy with no significant Al depletion. A third β -NiAl alloy containing 0.1 at % Zr but with 10% less Al than the stoichiometric alloy was also tested and showed some depletion of Al, but the protective Al ₂ O ₃ /NiAl ₂ O ₄ was still maintained to close to 2700 hours. Zirconium SCALE SPALLING COMPUTER MODELING					
17. Key Words (Suggested by Author(s)) Cyclic oxidation; β -nickel aluminate; Zirconium effect; Scale spalling; Computer modeling			18. Distribution Statement Unclassified - Unlimited Subject Category 26		
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No of pages 18	22. Price* A03

